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Observation of hyperfine structure and isotope shift in autoionizing states

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We report the first observation of hyperfine structure and isotope shift in autoionizing states. This structure was investigated in the $5d_{3/2}nf$ $J=4,5$ ($n=36$–40) barium Rydberg series, excited from the recently localized metastable $5d^2\,{}^1G_4$ level. An isotope-selective detection method was used in a cw laser spectroscopic experiment on a collimated atomic beam. The experimental data provide valuable additional information for the analyses of these doubly excited series.

Theoretical studies, e.g., by Fano[1] have led to the prediction that in two-electron atoms due to strong correlations in the electronic motions long-lived doubly excited states of high energy may exist. The experimental investigation of these high-lying doubly excited states requires multistep laser excitation using bound Rydberg or autoionizing states as intermediate levels.[2] Efforts to populate these strongly correlated states are undertaken in several laboratories.[2–4] A profound knowledge of the wave functions of the intermediate states is indispensable for the interpretation of the experimental results pursued. In the determination of wave functions of interacting Rydberg series converging to the same ionization limit observables other than energies of fine-structure levels are needed. These observables can be hyperfine structure, isotope shifts, g_J factors, lifetimes, and angular distributions of emitted electrons. For bound series, hyperfine structure (HFS) and isotope shifts (IS) are often used.[5]

Generally autoionizing atomic states have lifetimes of the order of picoseconds yielding broad resonances in the frequency domain. These broad autoionization line profiles prevent the observation of small effects such as isotope shifts and hyperfine structure. In this case autoionizing linewidths and angular distributions of the emitted electrons have to be analyzed.[6] However, for states with high total angular momentum (J) a measurement of these angular distributions and their fit to theory may become very difficult due to, e.g., the complicated form of the angular distribution. The information, which can be extracted from linewidths alone, is rather limited.

In the alkaline-earth elements in many cases autoionizing states with high J values ionize slowly. The reason is that the autoionization process of such states requires a change in angular momentum of the ionic core larger than one. Recently we observed extremely narrow autoionization linewidths (down to a Dopler-limited 10 MHz) in the $[5d_{3/2}nf]$ $J=4,5$ series in atomic barium.[7] Two $J=4$ ($5d_{3/2}nf_{5/2,7/2}$, with quantum defects 0.12 and 0.10) and one $J=5$ ($5d_{3/2}nf_{7/2}$, with quantum defect 0.07) Rydberg series are converging to the second ionization limit in barium ($5d_{3/2}$) and are autoionizing into the $6s\epsilon l$ continua. Transitions from the $5d^2\,{}^1G_4$ level to $5d_{3/2}nf$ $J=3$ states were too weak to be studied systematically. Weak interactions with series converging to the slightly higher $5d_{5/2}$ limit were observed.[7] These states appear to be suitable intermediate states for excitation to higher-lying doubly excited states.

In the present experiment we have measured for the first time, in addition to known energy values, isotope shifts, and hyperfine structure of the ^{137}Ba isotope (nuclear spin $I=\frac{3}{2}$) in several unperturbed $5d_{3/2}nf$ $J=4,5$ states. The observation of HFS and IS shifts in these states was hampered by the dominant signal of the most abundant ^{138}Ba and ^{136}Ba isotopes. This problem was solved with the use of a quadrupole mass filter to resolve the signals of the different isotopes. In the experiment, a collimated beam of barium atoms is orthogonally intersected by the output beam of a stabilized ring dye laser (bandwidth 1 MHz) using the dye stilbene 3. The $5d_{3/2}nf$ $J=4$ and $J=5$ states are excited from the $5d^2\,{}^1G_4$ metastable level at 24696.278(4) cm^{-1} which is populated by electrons emitted from a hot tungsten filament in front of the barium-filled tantalum oven. The quadrupole mass filter, detecting the ions produced in the autoionization process, is positioned directly behind the interaction region. The signal, together with the calibration signal from

a 75-MHz etalon is stored on a microcomputer, which also controls the laser scan. This experimental setup with the exception of the mass filter is described elsewhere.[8]

Suitable states for the study of hyperfine structure in the $5d_{3/2}nf$ series are preferably unperturbed by $5d_{5/2}n'l$ states and have minimal linewidths. For this reason, spectra of the following states were recorded: $[5d_{3/2}nf_{7/2}]$ $J=5$, $n=36$–40; $[5d_{3/2}nf_{5/2,7/2}]$ $J=4$, $n=35$–40; and a state of which the J assignment was uncertain, $[5d_{3/2}30f]$ $J=4$ or 5. In Fig. 1 two typical spectra of a $5d_{3/2}nf$ $J=5$ state are shown. The first (upper) spectrum is obtained by observing the emitted electrons, thus showing contributions from all isotopes. The second (lower) spectrum is obtained using mass selective detection. Obviously, the resolution of the quadrupole mass filter is sufficient to allow the observation of the signal of a single isotope. In the spectra of the $J=5$ states all transitions with a change in the hyperfine quantum number (F) of $\Delta F=1$, and most transitions with $\Delta F=0$, were observed. As the transition to the $J=5$ states is from a $J=4$ metastable state, the $\Delta F=-1$ transitions are weakest, thus making their observation difficult. In the spectra of the $J=4$ states all $\Delta F=0$ transitions were observed at all values of n except at $n=35$, where observation of some transitions was hampered by background signal originating from the $5d^2\,{}^3F_4$ to $5d_{3/2}6f$ $J=4$ transition. Most of the $\Delta F=1$ and -1 transitions were also observed in the $J=4$ case. Using the known $5d^2\,{}^1G_4$ state hyperfine structure splitting[8] all observed lines could be assigned unambiguously. This assignment is consistent with observed line strengths and J-value assignments made previously.[7] The $5d_{3/2}30f$ state turned out to be $[5d_{3/2}30f_{7/2}]$ $J=4$.

The hyperfine structure of the studied levels as well as the single fine-structure transition of the ^{138}Ba isotope are shown in Figs. 2–4 relative to the center of gravity of the hyperfine structure in the metastable state. Direct results of this analysis are improved values for the hyperfine constants A and B of the $5d^2\,{}^1G_4$ level (see Table I). As is evident from Fig. 2 the HFS of the $J=5$ states is unperturbed. A detailed inspection of the data reveals a gradual change in position of the $F=\frac{7}{2}$, $\frac{9}{2}$, and $\frac{11}{2}$ levels which shows the effect of the decreasing fine-structure energy splittings with increasing principal quantum number n. In Fig. 3 the HFS of the $J=4$ states with defect 0.10 is shown. Again there is no observable effect of perturbations induced by other Rydberg series. Here, however, a more pronounced change in position of the $F=\frac{5}{2}$, $\frac{7}{2}$, and $\frac{9}{2}$ levels is visible. This is mainly the effect of decreasing separation with the otherwise unobserved $5d_{3/2}nf$ $J=3$ fine-structure level. In Fig. 4 the HFS of the $J=4$ levels at defect 0.12 is plotted. It shows, apart from the aforementioned effects, the influence of a perturbing state at $n=38$. This perturber is a $J=3$ state as may be deduced from the fact that the $F=\frac{11}{2}$ states are not affected. Although the perturbing state itself is not observed it is most probably a $5d_{5/2}15p$ $J=3$ state. In both $5d_{3/2}40f$ $J=4$ states the complete hyperfine quadruplet is shifted 10 MHz. This shift is induced by the nearby

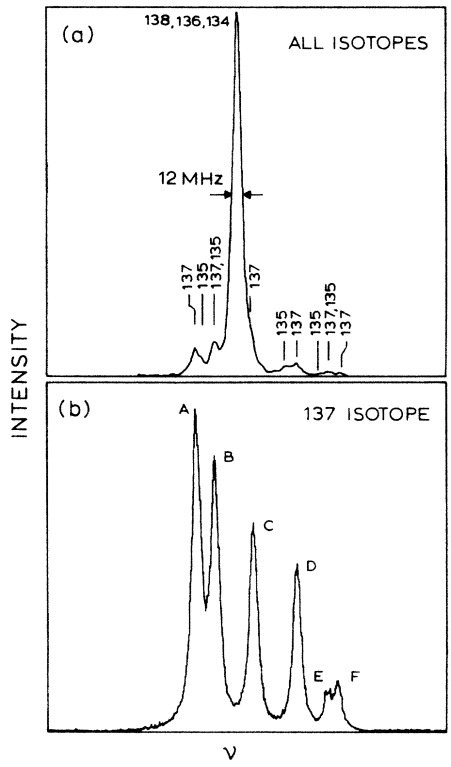

FIG. 1. Hyperfine structure of $5d_{3/2}39f_{7/2}$ $J=5$. (a) Signal of all isotopes. (b) ^{137}Ba isotope signal only; the transitions indicated are A: $F=\frac{11}{2}\rightarrow F=\frac{13}{2}$; B: $F=\frac{9}{2}\rightarrow F=\frac{11}{2}$; C: $F=\frac{7}{2}\rightarrow F=\frac{9}{2}$; D: $F=\frac{5}{2}\rightarrow F=\frac{7}{2}$; E: $F=\frac{9}{2}\rightarrow F=\frac{9}{2}$; F: $F=\frac{11}{2}\rightarrow F=\frac{11}{2}$ and $F=\frac{7}{2}\rightarrow F=\frac{7}{2}$.

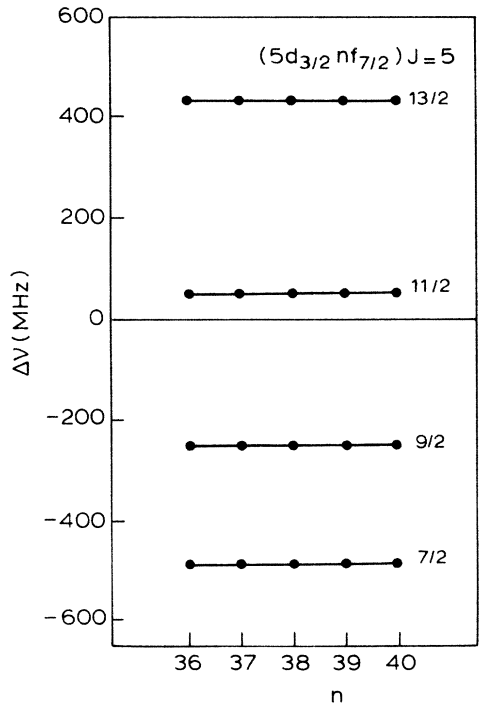

FIG. 2. Hyperfine positions for the $5d_{3/2}nf_{7/2}$ $J=5$ level as a function of n relative to the center of gravity of the hyperfine structure in $5d^2\,{}^1G_4$.

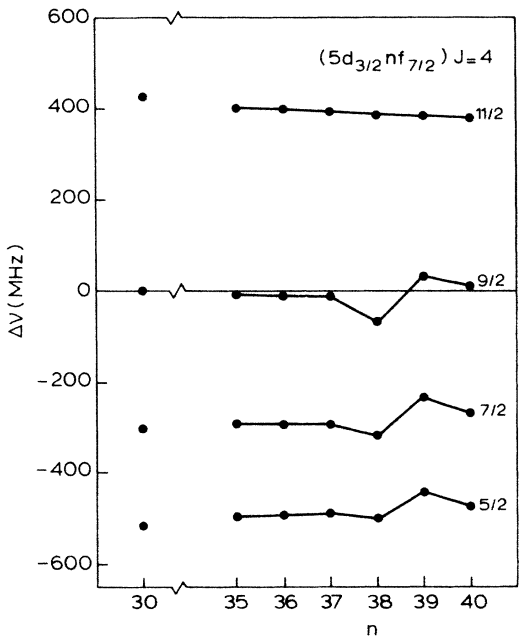

FIG. 3. Same as in Fig. 2 for the $5d_{3/2}nf_{7/2}$ $J=4$ level.

$5d_{5/2}15p_{3/2}$ $J=4$ state.

To determine the composition of the wave functions of the $5d_{3/2}nf$ $J=4$ levels, all experimental positions of the hyperfine states with the same F value in the $5d_{3/2}nf$ multiplet are needed. As we were unable to observe the $5d_{3/2}nf$ $J=3$ levels with hyperfine components $F=\frac{3}{2}$, $\frac{5}{2}$, $\frac{7}{2}$, and $\frac{9}{2}$, only the $F=\frac{11}{2}$ levels are available for this

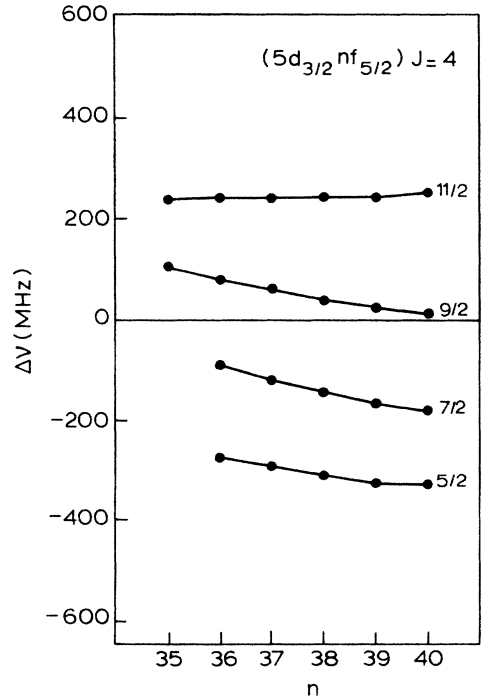

FIG. 4. Same as in Fig. 2 for the $5d_{3/2}nf_{5/2}$ $J=4$ level.

TABLE I. The hyperfine splitting of the $5d^2\,{}^1G_4$ level of ^{137}Ba (errors correspond to one standard deviation) and the corresponding A and B factors.

F-F'	$\nu(F)-\nu(F')$ (MHz)	A (MHz)	B (MHz)
$\frac{11}{2}$ - $\frac{9}{2}$	331.8(0.4)	49.83(0.06)[a]	84.2(0.5)[a]
$\frac{9}{2}$ - $\frac{7}{2}$	204.3(0.4)	50.0(0.2)[b]	83.5(1.5)[b]
$\frac{7}{2}$ - $\frac{5}{2}$	116.3(0.6)		

[a]Present experiment. [b]Reference 8.

purpose. The energies of these levels are calculated by diagonalizing the total energy matrix. This matrix is set up in the basis

$$|1\rangle = |5d_{3/2}nf_{7/2}\ J=5\rangle,$$

$$|2\rangle = \alpha|5d_{3/2}nf_{7/2}\ J=4\rangle + \beta|5d_{3/2}nf_{5/2}\ J=4\rangle,$$

$$|3\rangle = \alpha|5d_{3/2}nf_{5/2}\ J=4\rangle - \beta|5d_{3/2}nf_{7/2}\ J=4\rangle,$$

where $|\beta| = (1-\alpha^2)^{1/2}$ and the wave functions $|1\rangle$ to $|3\rangle$ are, respectively, the pure fine-structure levels belonging to the $5d_{3/2}nf$ $J=5$ series at quantum defect 0.07, the $5d_{3/2}nf$ $J=4$ series at 0.10, and the $5d_{3/2}nf$ $J=4$ series at quantum defect 0.12. The zero-order energies are chosen to be the experimental fine-structure energies of the even ^{138}Ba isotope, as the positions of the hyperfine states are known relative to the ^{138}Ba component in the transition.

The calculated hyperfine energies can be fitted to experimental data with two free parameters:[9] β is the mixing coefficient and $\delta\nu$ is a shift parameter which takes into account the difference in transition frequencies for the ^{138}Ba and ^{137}Ba isotopes. The hyperfine matrix elements are easily calculated as the contribution from the $5d_{3/2}$ electron is known accurately.[10] The contribution of the nf electron is neglected as the HFS interaction scales with $\langle n^{-3}\rangle$. The results of the fitting procedure are collected in Table II, implying even for unperturbed $5d_{3/2}nf$ $J=4$ states that neither jj nor jl coupling is appropriate. As in jj coupling, the β parameter is smallest when we give an assignment of $5d_{3/2}nf_{5/2}$ $J=4$ for the series at defect 0.12 and $5d_{3/2}nf_{7/2}$ $J=4$ for the series at defect 0.10. This differs from the earlier assignment[7] which was mainly based upon *ab initio* Hartree-Fock calculations. Furthermore these results determine the multichannel quantum defect theory (MQDT) parameter describing the interac-

TABLE II. The mixing coefficient β and the shift parameter $\delta\nu = \delta\nu_{\rm TIS}^{138,137}$ as a function of the principal quantum number n. (Errors correspond to one standard deviation.)

n	β	$\delta\nu$ (MHz)
36	+0.3814(0.0001)	+6.5(0.7)
37	+0.3981(0.0037)	+6.5(0.7)
38	+0.4249(0.0005)	+9.3(0.7)
39	+0.4304(0.0004)	+8.6(0.6)
40	+0.4544(0.0001)	+7.7(0.9)

tion between the two $5d_{3/2}nf\ J=4$ channels.

Because of the symmetry in this particular diagonalization problem, there is an ambiguity in the sign of the parameter β. To remove this ambiguity the relative intensities of the two $5d_{3/2}nf\ J=4$ fine-structure states excited from the $5d^2\,{}^1G_4$ metastable state were calculated using standard LS transition rules. To obtain agreement with the experimentally observed relative intensities a small amount of $^3F_4$ character must be added to the wave function of the $5d^2\,{}^1G_4$ state. A $^3F_4$ admixture varying between 0.0 and +0.07 was found from the observations at different n values. The sign of the $5d_{3/2}nf\ J=4$ mixing coefficient β came out as indicated in Table II. As expected, the $^3F_4$ admixture in the $5d^2\,{}^1G_4$ state is small as this state has a lifetime of at least several milliseconds and lies 939.25 cm^{-1} above the $5d6p\ {}^3F_4$ state.

The values of the shift parameter $\delta\nu$ obtained from the fitting on the $5d_{3/2}nf\ F=\frac{11}{2}$ hyperfine states are directly related to the transition isotope shift (TIS) $\delta\nu_{\mathrm{TIS}}^{138,137}$. By comparing the spectra of the 137 isotope with the mass filter slightly detuned towards the 136 or 138 isotope $\delta\nu_{\mathrm{TIS}}^{138,136}$ has been measured. The result for $\delta\nu_{\mathrm{TIS}}^{138,136}$ is 2.0(2.0) MHz. These transition isotope shifts were also calculated using methods similar to those used in Ref. 6 [here the $5d8p\ {}^1F_3$ residual isotope shift (RIS) is assumed to be equal to the $5dnl$ RIS]. These calculations resulted in a value of $-1(10)$ MHz for $\delta\nu_{\mathrm{TIS}}^{138,136}$ and $-24(14)$ MHz for $\delta\nu_{\mathrm{TIS}}^{138,137}$. As is evident from Table II, the experimental values for $\delta\nu_{\mathrm{TIS}}^{138,137}$ are significantly higher than the calculated value, which indicates a difference between the $5d8p\ {}^1F_3$ RIS and $5dnf$ RIS.

In summary, hyperfine structure and isotope shifts have been observed in autoionizing states for the first time. It is demonstrated that HFS is an important observable for the determination of the wave function of these states. This opens up the possibility to make a more complete multichannel quantum-defect theory analysis of autoionizing Rydberg series. In our laboratory two-step laser excitation experiments to populate $nfn'f$ doubly excited states from the metastable $5d^2\,{}^1G_4$ via autoionizing $5dnf$ levels in barium are in preparation. The present results are expected to be extremely important for future data analysis.

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